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ION SELECTIVE ELECTRODES IN WATER QUALITY ANALYSIS

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The condition of our drinking water has received considerable attention recently, and we are becoming increasingly more aware that some of the pollutants or low level chemicals might be potentially hazardous to our health. The Water Supply Research Division is constantly promoting a high standard of excellence in the quality of water consumed by the Nation. Our research efforts will help pave the way for advances in the art of drinking water treatment and will combat, minimize and eventually eliminate all hazards to health derived from drinking improperly treated water.

One of the most effective ways to insure water quality is to maintain a constant check on its condition. The work presented in this report illustrates one aspect of continuous water quality examination; namely by ion selective electrode.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

The maintenance of water quality whether at the treatment plant or out in the distribution system is predicated on accurately knowing the condition of the water at any particular moment. Ion selective electrodes have shown tremendous potential in the area of continuous water quality analysis, and were employed by the Water Supply Research Division's Mobile Water Quality Laboratory to monitor: alkalinity, calcium, chloride, fluoride, hardness, nitrate, and pH.

The pH and the chloride electrodes were housed in a commercial unit and linked to the computer with a minimum number of operating problems. The other parameters required more development and all relied on ionic strength or pH buffers to swamp out problems of activity and ionic strength. The test periods were usually about a week in length, and data was presented as to the reliability and accuracy of the electrodes.

It was found that the electrodes performed quite well, and when compared to accuracy statistics found in Standard Methods for the Examination of Water and Wastewater, the electrode methods were in the same region.

INTRODUCTION

Recently, the news media have kept the public informed about several important episodes in the controversy over drinking water quality and public health. A notable instance is the finding of asbestos fibers and/or chlorinated organics in some water supplies. As a direct result of receiving this type of information, the public has become more knowledgable about the quality of drinking water and its associated problems. Many people became aware that the water taken for granted for so many years may not be as pure and wholesome as was once thought.

Some of the chlorinated hydrocarbons, thought to be cancer-causing agents and, paradoxically, appearing as a result of the disinfection process--chlorination[1]--are undesirable in a drinking water system, and research has been undertaken to eliminate the problem. Another problem associated with water quality, but without as much public recognition, is the deterioration of drinking water as it travels through the distribution system. Consumers commonly think that quality water leaving the treatment plant will arrive at its destination having the same quality. In a few cases this assumption is correct, but for many users the water can arrive significantly changed in quality. Examples are the dissolution under certain conditions of metals such as lead, iron, zinc, and cadmium as well as the loss of asbestos fibers from asbestos-cement pipes.

The traditional approach to water quality analysis has involved grab sampling and transportation to the laboratory for subsequent work. This approach has the disadvantages associated with grab sampling, namely, representative samples, necessary preservation, and changes caused by transportation conditions (temperature, sunlight, travel time, etc.). To circumvent many of these problems, some groups have installed analytical equipment on trucks and moved the laboratory into the field for on-site analysis. However, on-site analysis does not answer the question of the validity of the results based on one sample. The ideal solution to the problem of sampling would be to install a field laboratory with the capability for continuous sampling as well as continuous analysis.

The Water Supply Research Division of the U.S. Environmental Protection Agency had assembled under contract with the National Sanitation Foundation a mobile water quality laboratory with the capability for continuous sampling and analysis. The laboratory is capable of monitoring 19 water quality parameters and, in most cases, provides a continuous record of the analysis of that parameter. Some parameters are semi-continuous in that the water sample is compared with a standard before the final result is recorded. All parameters are sampled and analyzed at least twice an hour. The purpose of this report is to describe certain aspects of this mobile monitor in detail.

Ion Selective Electrodes

One of the best ways to continuously analyze for a particular substance is to use an electrochemical sensor, and the best electrochemical sensors are known as electrodes. There are many types of electrodes, and one of the types employed on the mobile laboratory was the specific ion electrode. Specific ion electrodes are a special type of sensor that can detect one type of ion in a mixture of many and report its concentration. These electrodes are receiving a great deal of attention in water quality analysis because of this discriminating ability.[2,6,19,38-41] Traditional analysis might require expensive spectrographic equipment or involved wet chemical analysis, while specific ion electrodes give rapid, sensitive, economical, continuous and reasonably accurate results. It was these attributes that led to their incorporation into the analytical systems of the mobile laboratory. The systems employing specific ion electrodes are: pH, alkalinity, chloride, fluoride, divalent hardness, calcium, and nitrate.

The operating principle for all specific ion electrodes revolves around the creation of a classical concentration potential across a permeable membrane, or simply stated, follows the Nernst Equation:

$$E = E^{\circ} + \frac{2.3\ RT}{Z\ F} \log [A^{+}] \qquad \text{Eq (1)}$$

where E equals the equilibrium potential, E° is the standard potential, $\frac{2.3\ RT}{F}$ is the Nernst Factor (59.16 mv 25°C), Z is the charge on the diffusing ion. The standard potential developed will depend on the choice of reference electrode as well as the internal reference solution. Equation (1) is thus a direct relationship between the activity of an ion and the potential it developed.

Activity is sometimes a difficult parameter to work with because a knowledge of the activity coefficient is necessary before the analytical concentration can be determined. Activity is related to concentration by the following equation:

$$A = \delta \times c \qquad \text{Eq (2)}$$

where A is the activity of the ion, δ is the activity coefficient and c = the concentration of the ion being measured. The activity coefficient is a function of ionic strength and can be determined by a modification of the Debye Huckel Equation:[42]

$$-\log \delta = Zi^{2} \left[\frac{0.511\ \sqrt{u}}{1 + 1.5\ \sqrt{u}} - 0.2\ u \right] \qquad \text{Eq (3)}$$

where δ is the activity coefficient, Zi is the charge on the i^{th} ion, and u is the ionic strength. If the value of u is sufficiently high due to the addition of an inert species, the contribution of ionic strength by the sample will be negligible. This technique of establishing a constant ionic strength is called swamping[41] and is used in many specific ion applications.[22,24,25,27,29,43,44] Constant ionic strength establishes that the activity coefficient will also be

constant. If the activity coefficient is constant, changes in activity will be directly reflected by changes in concentration of the ion of interest, or the equilibrium potential will be indicative of the concentration of the specific ion.

EXPERIMENTAL

The Apparatus and reagents used on the mobile laboratory are listed by parameter in alphabetical order. All the systems were supplied reagents by a Technicon II Proportioning Pump and the data collected and processed by a Texas Instruments 960A Minicomputer. The switching between baseline and sample was handled by Valcor thru-way miniature "dri-solenoid" valve, series SV-72, and supervised by the computer.

Alkalinity

Apparatus:

A conventional combination pH electrode, Sargent No. S-30070-10, was used in conjunction with its flow cell to determine alkalinity. A Radiometer pHM Research pH meter was used with a 7100 series Hewlett Packard recorder, to monitor and record the alkalinity.

Reagents:

A buffer solution of 0.05 M Potassium Hydrogen Phthalate (KHP) and 0.019 M HCl was prepared by mixing 91.8 g KHP and 13.4 mℓ con HCl in 9 ℓ of distilled water. The pH was adjusted, if necessary, with con HCl to 3.15.

A baseline solution of 0.95310 g of Na_2CO_3 was dissolved in one liter of distilled water. Two hundred milliliters of this solution was diluted to 9 ℓ and was equivalent to 20 mg/ℓ alkalinity as $CaCO_3$.

Calcium

Apparatus:

An Orion 93-20 Calcium Selective Ion Electrode was used to determine calcium hardness. The electrode was used in a custom made flow cell with a Sargent, S-30080, Miniature Calomel Electrode. An Orion 801A Research pH Meter monitored the calcium and it was recorded on an Esterline Angus L11025 dual channel recorder.

Reagents:

A buffer solution was prepared in the same manner as described in Standard Methods[13] p 181 but diluted 38 mℓ to 100 mℓ. The resulting solution had nearly the same pH, 10.1, but the ionic strength was reduced from 11.4 M to 4.275 M.

An additional Ammonia Chloride-Ammonia Hydroxide buffer was prepared to have a pH of 9.0 and an ionic strength of 0.60 M.

A baseline solution was prepared by spiking tap water with about 200 mg/ℓ of calcium expressed as $CaCO_3$.

Chloride

Apparatus:

A Beckman 19521 Silver-Silver Chloride billet type electrode was used in conjunction with a Beckman 19730 Palladium Junction reference electrode to determine chloride ion concentrations. The electrodes were housed in a plastic flow cell located in a Schneider Robot Stream Monitor, and the data recorded on an Esterline Angus Multipoint Recorder.

Reagents:

Potassium chloride standards were prepared to have concentrations of 35, 88, and 177 mg/ℓ chloride. These solutions were made by diluting 0.01 M KCl and were also used for standardization of the conductivity cell.

Free Fluoride

Apparatus:

An Orion No. 94-09A Fluoride Ion Electrode was used with a Sargent No. S-30080 Miniature Calomel Electrode to determine free fluoride ion concentrations. A Leeds and Northrup No. 7415 Research pH Meter was used with a Linear Instruments No. 297 dual channel recorder to observe and record the fluoride data.

Reagents:

A buffer solution of 8.14 mℓ (0.1 M) Acetic Acid, 121.41 g (1.0 M) Sodium Nitrate were dissolved in 1 ℓ of distilled water and the pH adjusted, if necessary, with NaOH. The ionic strength of this buffer was kept about 1.1 M.

A baseline solution was prepared by diluting (1:100) a commercial standard for fluoride (0.1 MO to a stock solution of 19 mg/ℓ F^- and subsequent dilution of the stock solution 105.3 mℓ to 20 ℓ to obtain a baseline solution of 0.1 mg/ℓ fluoride.

Total Fluoride

An Orion No. 94-09A Fluoride Ion Electrode was used in conjunction with a Sargent No. 30080 Miniature Calomel electrode for the Total Fluoride determination. An Orion 801A Research pH Meter was used in conjunction with a Linear Instruments No. 297 dual channel recorder for monitoring and recording the data.

Reagents:

A buffer solution of 16.29 mℓ (0.2 M) Acetic Acid, 85.0 g Sodium Nitrate (0.7 M) and 84.0 g (0.2 M) Sodium Citrate were dissolved in 1 ℓ of water and the pH adjusted, if necessary, with NaOH. The ionic strength of the buffer was also about 1.1 M.

Baseline:

The same baseline solution used for Free Fluoride was also used for total fluoride.

Hardness:

An Orion 93-32 Divalent Hardness Specific Ion Electrode was used in conjunction with a Sargent 30080 Miniature Calomel reference electrode to determine the hardness of the water samples. A Corning 101 Research pH meter was used with the Esterline Angus L11025 recorded to monitor and record the data.

Reagents:

A buffer solution was prepared in the same manner as described in Standard Methods[13] p 181, but diluted 18.75 mℓ to 100 mℓ. The resulting solution had a pH of about 10.1 but the ionic strength was reduced from 11 M to 2.14 M.

The baseline solution used was the same solution used for the calcium baseline, with total hardness being about 200 mg/ℓ higher than the tap water.

pH

Apparatus:

A Beckman 19500 general purpose glass electrode was used in conjunction with a Beckman 19730 Palladium Junction reference electrode to measure hydrogen ion concentration. The electrodes were located in the Schneider Robot Stream Monitor and the data was collected on a Esterline Angus Multipoint recorder.

Reagents:

Commercial buffers of pH 7 and 10 were used for the calibration of the electrode.

Nitrate

An Orion 93-07 Nitrate Ion Electrode was used in conjunction with a Sargent S-30080 Miniature Calomel single junction electrode. A Corning research pH meter 112 was used to monitor the nitrate electrode and the data was collected on a 7100 series Hewlett Packard dual channel recorder.

Reagents:

A nitrate standard of 100 mg/ℓ N was prepared by dissolving 721.8 mg of anhydrous KNO_3 in 1 liter of distilled water. Working standards of 0.1 to 1.0 mg/ℓ N were prepared by dilution.

The baseline was prepared by adding about 1.0 mg/ℓ N to tap water.

The ionic strength adjustor was prepared by dissolving sodium fluoride in distilled water to make a solution of 0.006 M.

RESULTS AND DISCUSSION

Alkalinity

Alkalinity is a combination of all the species in water that will accept protons, and is usually comprised of bicarbonate, carbonate, and hydroxide. Alkalinity can be expressed by summing all the components in the system and expressing it as an equivalent of the protons accepted.[14]

$$[2H^+] = [HCO_3^-] + [CO_3^=] + [OH^-] \qquad \text{Eq (3)}$$

Thomas and Lynch[15] suggest that alkalinity is the capacity of a water to neutralize acidity up to the equivalence point. Regardless of how it is stated, alkalinity is an important water quality parameter, and is utilized by treatment personnel for regulating scaling or corrosion tendencies as well as pH, taste, and odor control.

A continuous system for monitoring alkalinity might well be patterned after the concept of the neutralizing capacity of water. If a buffer system of known hydrogen ion concentration is mixed with a known amount of water sample, the resulting change in hydrogen ion concentration will be a measure of the extent to which protons were accepted or simply the alkalinity of the water. The method used involved the mixing of a potassium hydrogen phthalate/hydrochloric acid buffer with tap water and the change in hydrogen ion concentration was determined as alkalinity.

Figure I illustrates the response of the phthalate buffer system to increases in alkalinity. Over the range of 20 mg/ℓ to 100 mg/ℓ alkalinity as $CaCO_3$, the relationship between pH and alkalinity was linear with a correlation coefficient of 0.997. This indicates that the system will behave in an accurate and precise manner for alkalinity values up to 100 mg/ℓ.

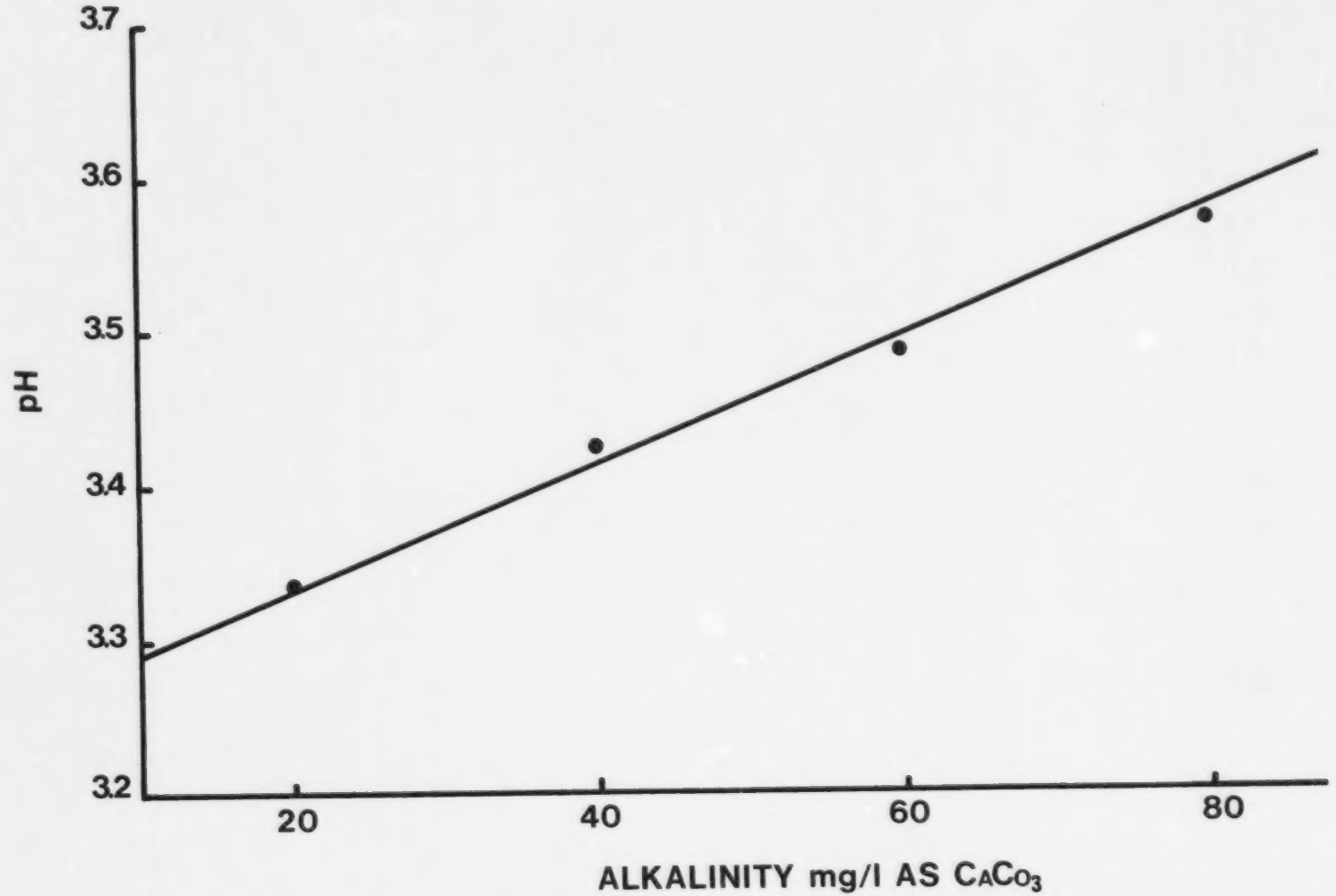

Figure 1. Relationship between pH and alkalinity.

After it was established that a linear relationship existed between changes in buffering capacity and alkalinity, the electrode was calibrated. Figure II shows the output from the alkalinity system as a function of alkalinity. The results of a least squares regression analysis shows a correlation coefficient of 0.998 and indicates a linear area of response between 20 mg/ℓ and 80 mg/ℓ of alkalinity.

The true test of any ion selective electrode employed in a continuous monitoring situation revolves around its long term reliability and accuracy. Therefore, after the electrode was calibrated it was placed on line analyzing a reservoir of the same tap water for an extended period of time. The electrode was operated for over 100 hours and analyzed about 270 samples. The results of this test are summarized in Figure III, with statistical information summarized in Table 1.

TABLE 1. STATISTICAL RESULTS OF THE ALKALINITY ELECTRODE

Mean	56.1 mg/ℓ
Standard Deviation	1.91
Relative Standard Deviation	3.4 %
Relative Error	1.6 %
Average Titration	55.2 mg/ℓ

Hardness and Calcium

Total hardness and calcium are parameters usually associated with the aesthetic considerations of drinking water, namely customer acceptance. However, they are also an important consideration to the water utility because their treatment could make large changes in their concentration and affect the corrosion or sealing tendencies, alkalinity, pH, and conductivity. Total hardness and calcium are also being considered as a possible agent in cardio vascular diseases.[16,17,18] Therefore, because of traditional and contemporary reasons, total hardness and calcium were incorporated as two of the parameters on the Mobile Laboratory.

Historically, hardness was determined by titration with a standard soap solution, but the subjectiveness of the endpoint cast some doubts on its accuracy. The development of EDTA titrations and indicators specific for hardness and calcium made contemporary analysis easy and accurate. However, titrations do not yield a continuous record of data, and since it was thought to be important to have continuous analysis it was decided to employ an ion selective electrode for divalent hardness and calcium. Ion selective electrodes have been used in hardness[23,30,41,43,45,49] and, calcium determinations[7,23,33-35,37,46,49] but little has been done in applying these electrodes to continuous analysis.[6,19,38]

The initial work on adapting hardness and calcium ion selective electrodes to continuous analysis involved standardizing the electrodes in distilled water standards, and directly inserting them into the sample stream.

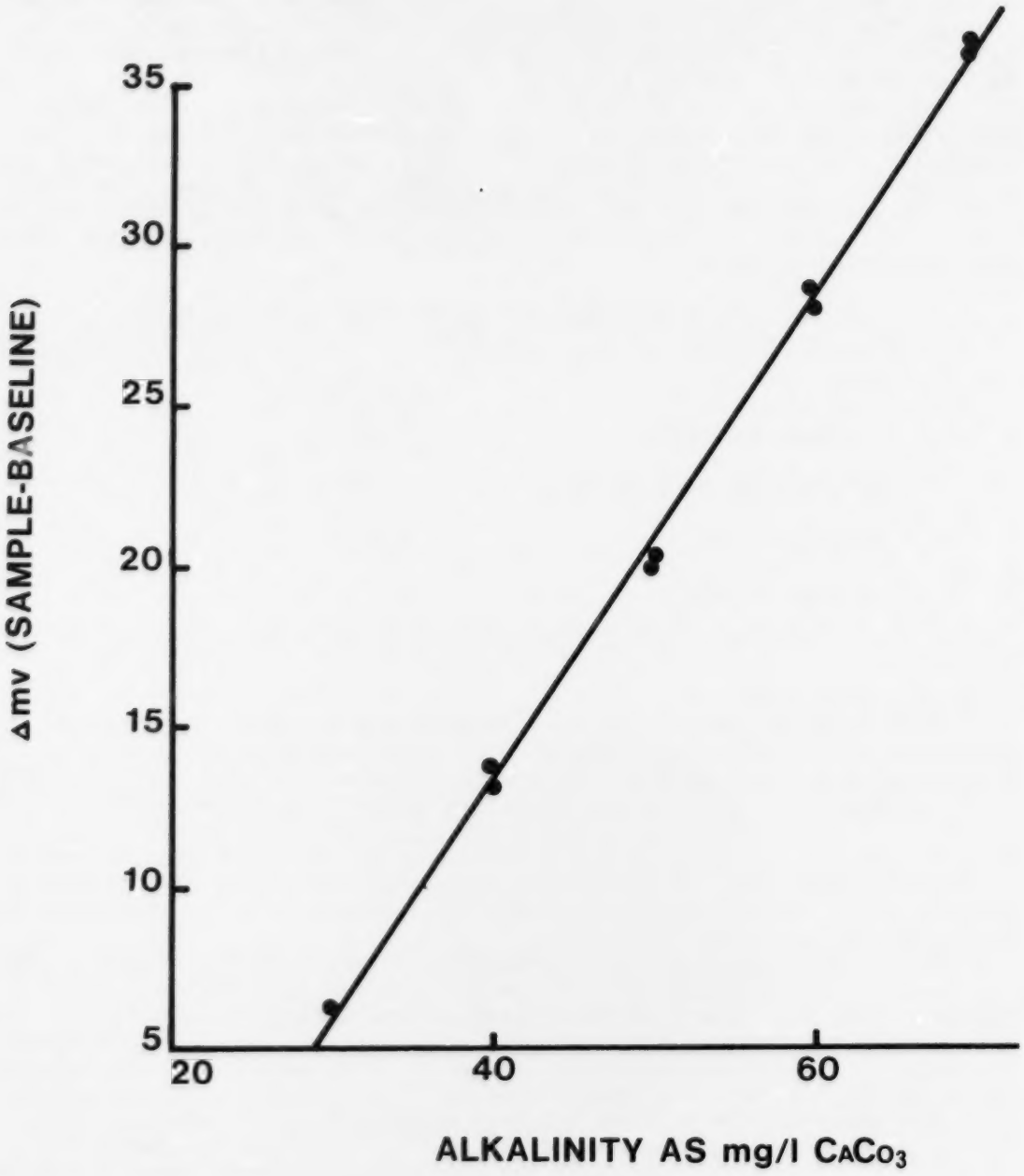

Figure 2. Alkalinity calibration curve.

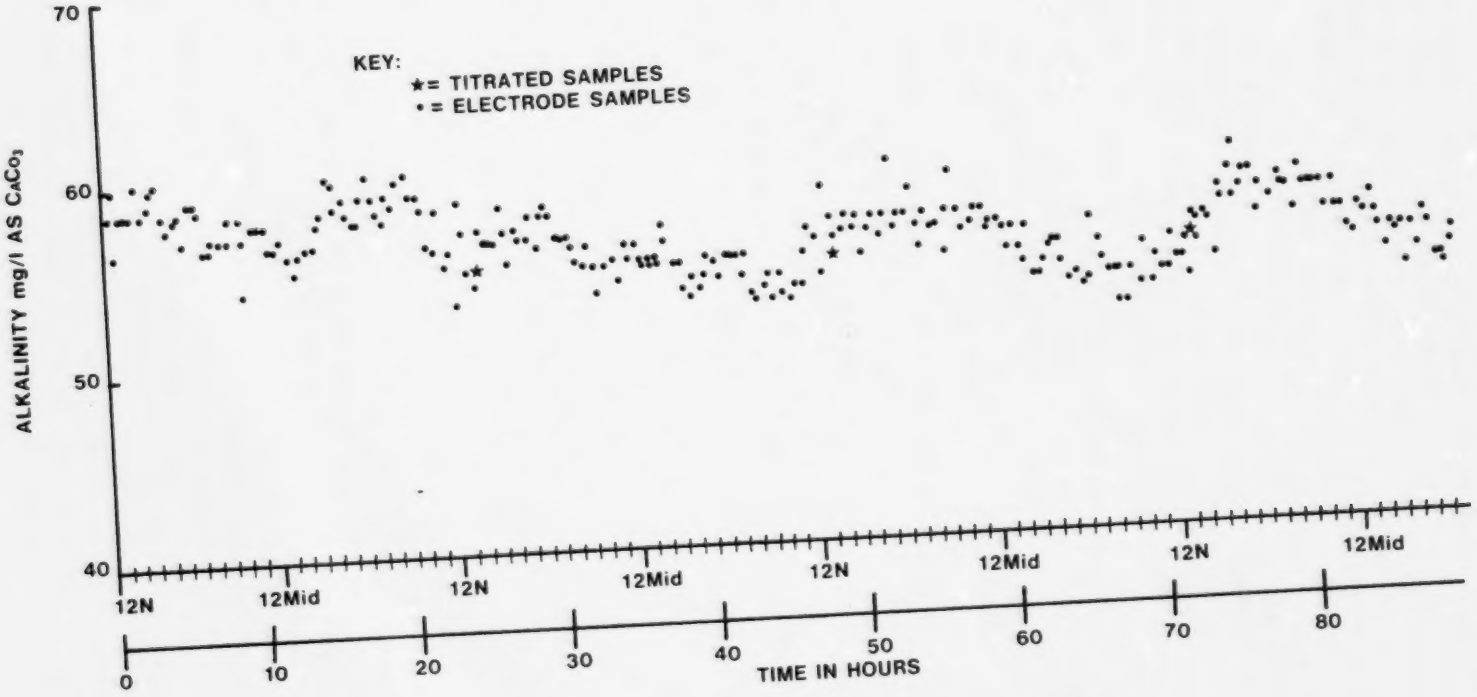

Figure 3. Performance of alkalinity electrode as a function of time.

The electrodes gave theoretical responses to the standards, but consistently gave low results on tap water. This agreed with published results,[19,45,50] and it was generally accepted that some degree of ion pair association was responsible for the lower readings. This problem can be overcome by using the technique of standard additions, and it was decided to adopt our system for hardness and calcium to a form of standard additions.

The Laboratory was to have national applicability, so a general system of standardization and analysis was needed. It was decided that to minimize any interferences inherent to the local water supply, the local tap water would be the baseline to which standard additions were made. It was also thought that ionic strength should be controlled more carefully. The selection of the appropriate ionic strength adjustor for hardness and calcium was a problem. Several investigators[45,46,47] have advocated the use of an inert salt with potassium chloride being one of the more promising. Therefore, a solution of potassium chloride was prepared to have a concentration of 7.0×10^{-2} moles/ℓ and was mixed with the standards. The data in Table 2 show the changes in ionic strength after the addition of potassium chloride, and any changes in potential due to ionic strength fluctuations should be drastically reduced.

TABLE 2. CHANGE IN IONIC STRENGTH OF STANDARDS MIXED WITH KCl

Calcium Concentration mg/ℓ	Ionic Strength of Standards moles/ℓ	Ionic Strength of Standards Mixed with KCl moles/ℓ
96	1.50×10^{-3}	1.32×10^{-2}
144	1.63 x "	1.33 x "
192	1.74 x "	1.34 x "
241	1.86 x "	1.35 x "
288	1.98 x "	1.36 x "

Figure IV shows the results of the calibration of the calcium electrode utilizing the potassium chloride ionic strength adjustor. The baseline to which the solutions were compared was tap water with a calcium hardness of 96 mg/ℓ as calcium carbonate. It can be readily seen that there was a great amount of scatter and a low value of 0.863 for the correlation coefficient of the least squares regression analysis.

Ruzicka and Tjell[7] suggest an ammonia chloride-ammonium hydroxide buffer for low levels of calcium in serum, and Standard Methods[13] uses the same kind of buffer for hardness titrations. The ammonium chloride-ammonium hydroxide buffer was prepared as stated in Standard Methods and substituted for the potassium chloride. A hardness electrode was used to evaluate this buffer by checking the response against ionic strength for a hardness standard of 233 mg/ℓ. The results of the study are summarized in Table 3.

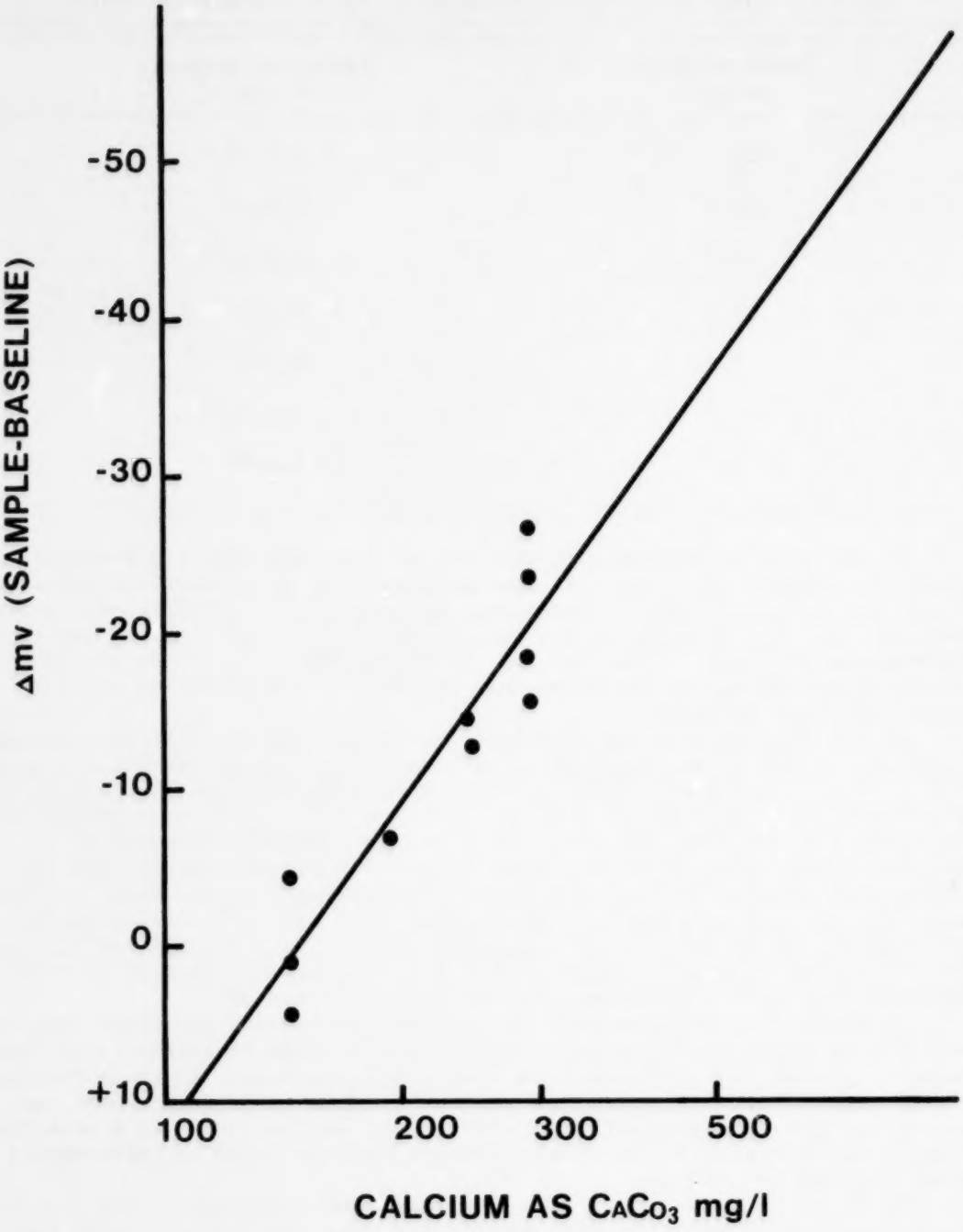

Figure 4. Calibration curve for the calcium electrode using 7.0×10^{-4}M KCl as the ionic strength adjustor.

TABLE 3. HARDNESS ELECTRODE RESPONSE TO IONIC STRENGTH OF BUFFER

Ionic Strength moles/ℓ	Electrode Response mv/mg/ℓ
11.4	0.0015
10.7	0.0024
9.5	0.0078
5.7	0.0084
2.9	0.0122
2.1	0.0159
1.4	0.0214

As the ionic strength was diluted, it was observed that the hardness electrode response increased. It was not shown, but as sensitivity increased, so did the background noise. Based on considerations of stability and signal response, an ionic strength of 2.1 moles/ℓ was selected as the best buffer for the hardness electrode. The same type of experiment was conducted for the calcium electrode and it was found that the optimum concentration was 2.9 moles/ℓ of ionic strength.

As was the case with the alkalinity electrode, the hardness and calcium electrodes needed to be evaluated for accuracy and reliability. The electrodes were calibrated using a standard addition of calcium chloride, but expressed as calcium carbonate. Figure V shows a calcium calibration for a series of standards 172, 224, 280, and 324 mg/ℓ as calcium carbonate compared to a baseline of 334 mg/ℓ. A least squares regression analysis gave a correlation coefficient of 0.995 indicating a linear relationship over the range calibrated. Figure VI shows a hardness calibration for a series of standards 216, 270, 309 and 358 mg/ℓ as calcium carbonate compared to a baseline of 357 mg/ℓ. A least squares regression analysis gave a correlation coefficient of 0.993 indicating a linear relationship over the range calibrated.

It should be noted here that the concentration of the tap water does not fall directly within the limits of calibration but must be extrapolated about 50 mg/ℓ. It has been shown that the electrodes were linear in their response over a range of about 200 mg/ℓ, and others[45,46] have shown them linear over several decades of concentration, therefore, it was reasonable to assume that a small extrapolation of the standard curves would be valid for determining total hardness and calcium.

After the hardness and calcium electrodes were calibrated, they sampled a large reservoir of tap water continuously for about 100 hours. During this time hardness and calcium tap water samples were repeatedly sampled about 270 times. During this sampling period the electrodes were periodically restandardized, and thus the data presented in Tables 4 and 5 are grouped according to restandardization.

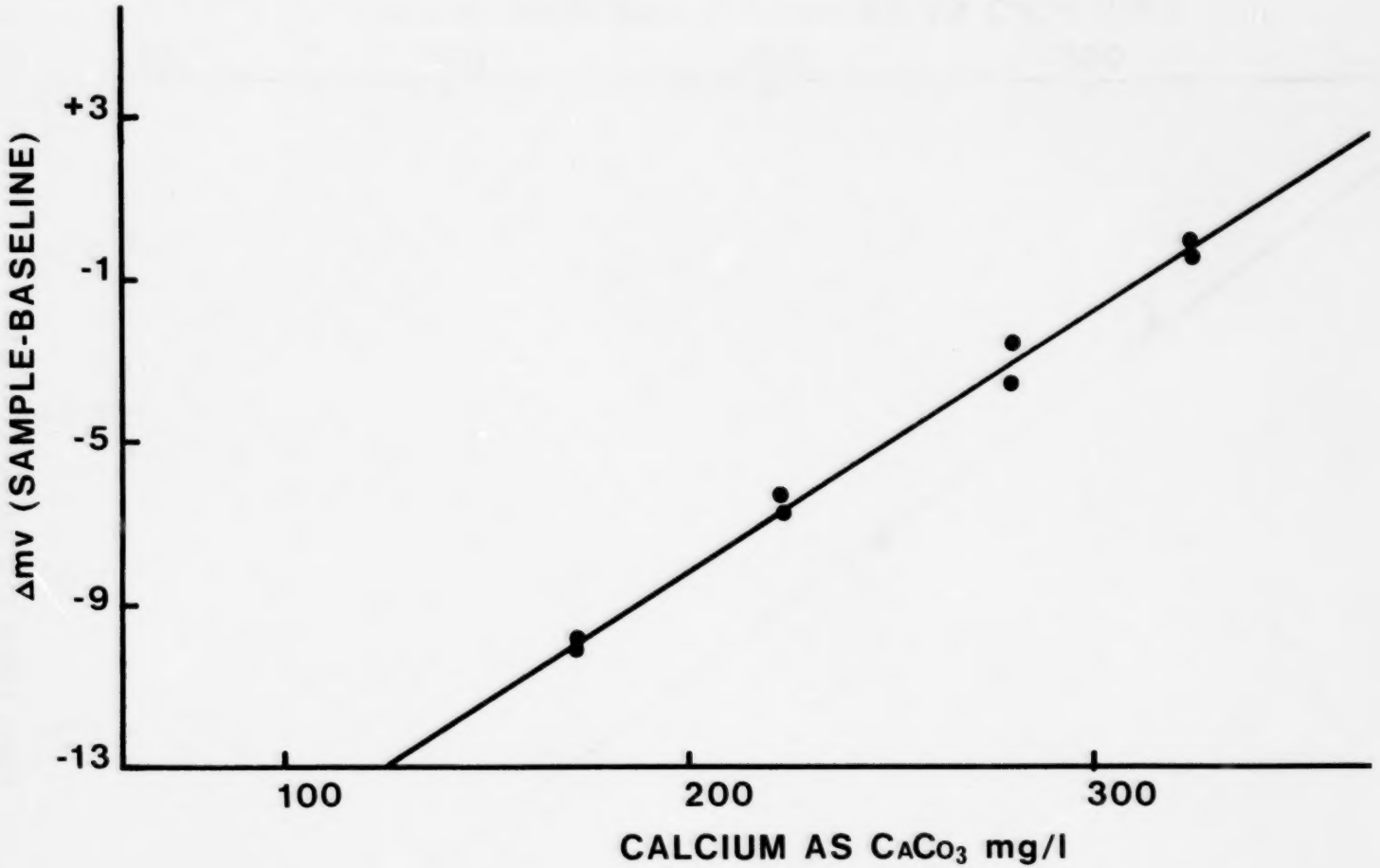

Figure 5. Calibration curve for calcium electrode in ammomium chloride - ammonium hydroxide buffer of 2.9 moles/l ionic strength.

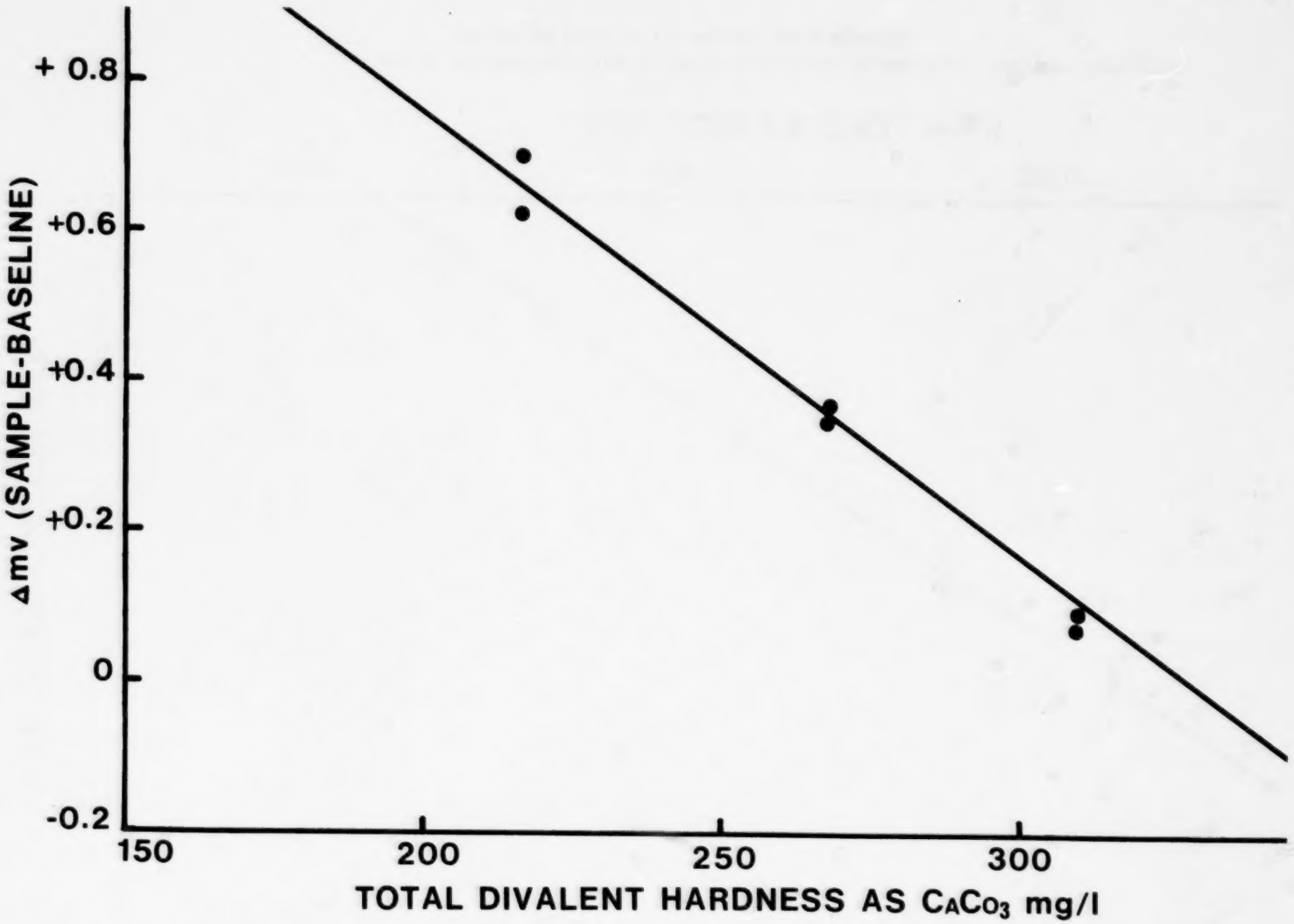

Figure 6. Total hardness calibration curve.

TABLE 4. STATISTICAL RESULTS OF HARDNESS ELECTRODE _____

Calibration Number	Mean	Standard Deviation	Rel. Std. Deviation	Relative Error	Titration
1	143 mg/ℓ	6.82	4.77 %	10.63 %	160 mg/ℓ
2	152 "	3.70	2.42 "	6.17 "	162 "
3	167 "	3.24	1.94 "	1.2. "	165 "
4	173 "	2.29	1.32 "	--	--

TABLE 5. STATISTICAL RESULTS OF CALCIUM ELECTRODE

Calibration Number	Mean	Standard Deviation	Rel. Std. Deviation	Relative Error	Titration
1	117 mg/ℓ	13.00	11.38 %	1.03 %	116 mg/ℓ
2	118 "	7.83	6.67 "	0.26 "	117 "
3	119 "	4.09	3.45 "	0.42 "	119 "
4	119 "	6.86	5.75 "	--	--

Figure VII shows a graphical summation of the long term study for total hardness and Figure VIII shows the same thing for calcium.

The ammonium chloride-ammonium hydroxide buffer helped to overcome problems of ionic strength by allowing the electrodes to respond to calcium and hardness activities while maintaining constant ionic strength. By swamping out some of the problems, the electrodes could be run at extended periods of time with reasonable precision and accuracy. However, there was one problem area of gradual calcium carbonate buildup that detracted from the method. Carbonate equilibrium diagrams[14] show that bicarbonate was converted to carbonate at a pH value of 10.4. The ammonium buffer's pH was 10.1 and it was thought that this would be sufficiently low to prevent bicarbonate conversion. However, a gradual buildup of calcium carbonate occurred along the inside of the system and became a problem especially around constrictions. After a two day induction period, both systems had to be flushed with 0.1 N HCl for about a half hour. This made the removal of the electrodes, shut down of the system, and recalibration necessary before it could be brought back on line.

It was clear that even though the buffer worked satisfactorily a change in pH was necessary. Utilizing the same chemicals, the pH was lowered to 9.0 and the ionic strength was reduced to 0.60 M. The same procedure of calibra-

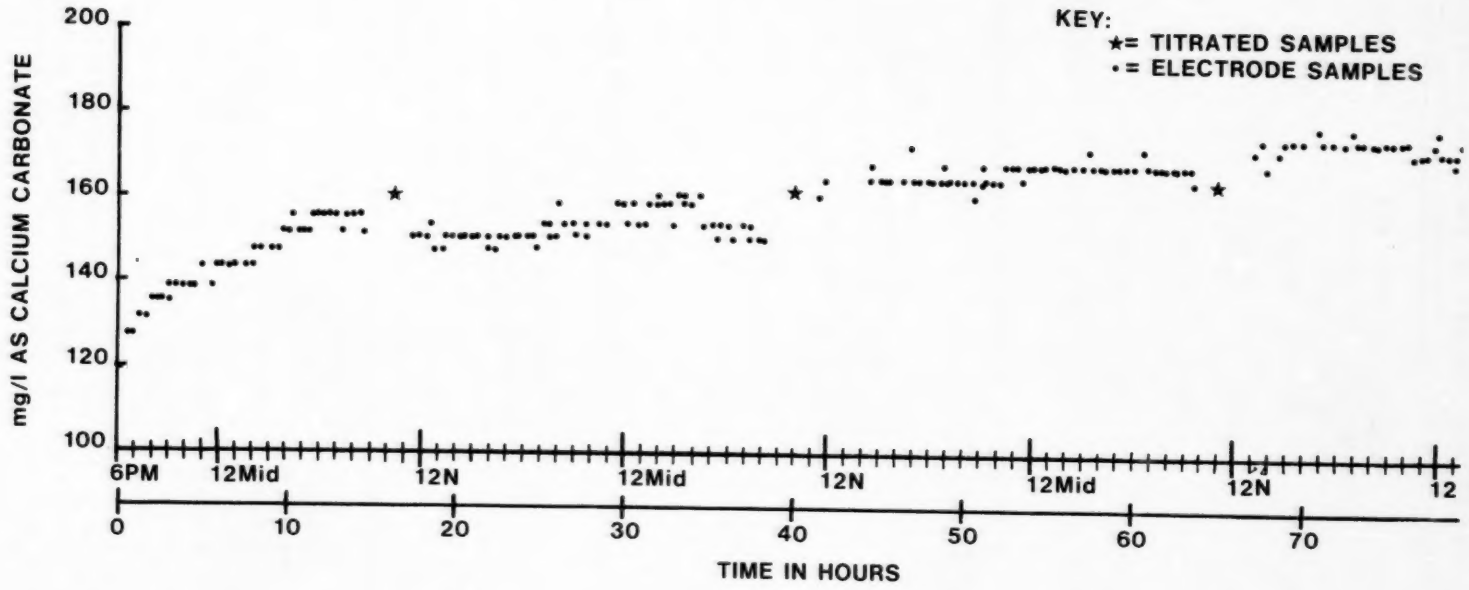

Figure 7. Performance of hardness electrode as a function of time.

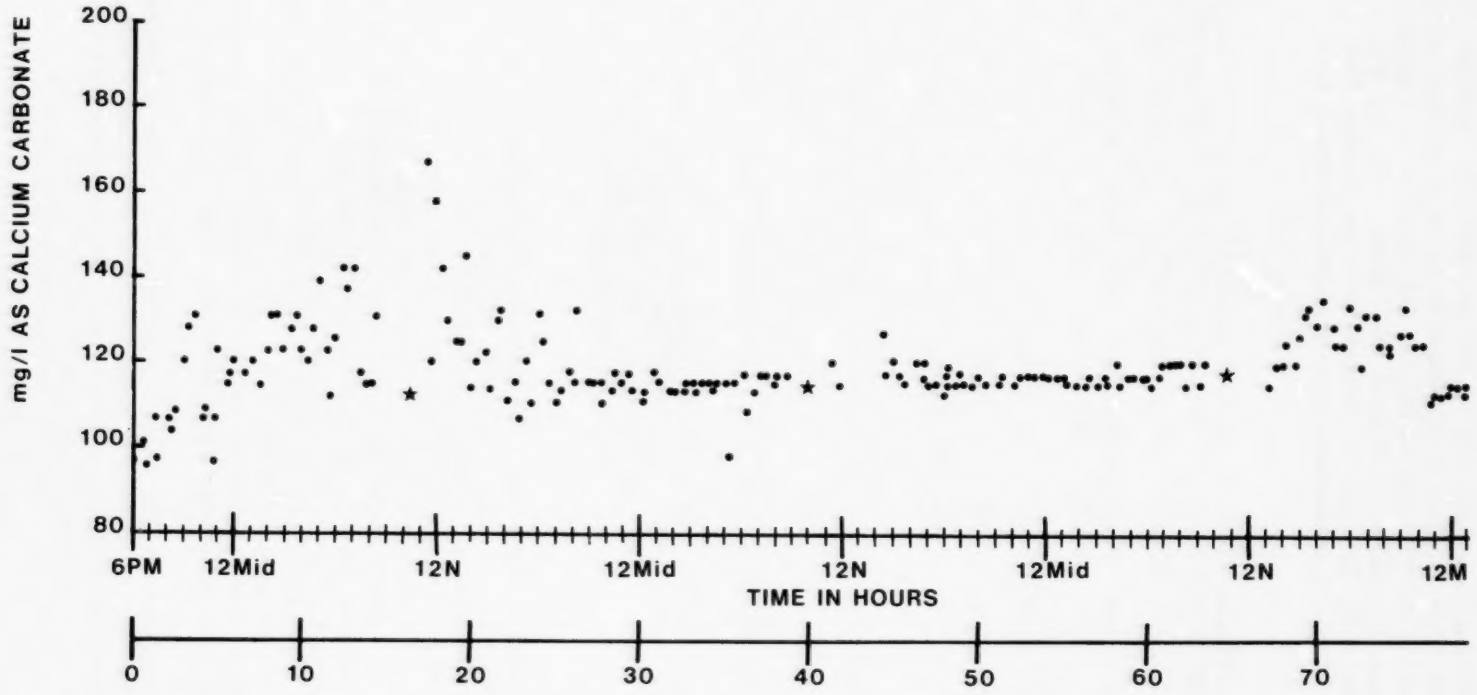

Figure 8. Performance of calcium electrode as a function of time.

tion and long term study was applied to the new buffer. However, there was one important difference in this study because it used online tap water rather than a large reservoir of the same sample. The results of the study for both calcium and hardness are shown in Figure IX. Since only one restandardization was done during the test the data is broken into two groups that correspond to each calibration. Table 6 summarizes the statistical results for the pH 9 buffer.

TABLE 6. STATISTICAL RESULTS FOR THE HARDNESS AND CALCIUM ELECTRODE UTILIZING THE 0.6 M AMMONIUM CHLORIDE-AMMONIUM HYDROXIDE BUFFER

Calibration Number	Electrode	Mean mg/ℓ	Standard Deviation	Rel. Std. Dev.	Relative Error	Average Titrated Value mg/ℓ
1	Hardness	175	7.99	4.37 %	1.16 %	173
2	"	165	2.90	1.76 "	2.42 "	170
1	Calcium	136	3.80	2.80 %	6.25 %	128
2	"	134	3.28	2.46 "	4.69 "	128

Studies on the calcium and total hardness electrode indicated that those parameters could be continuously monitored for extended periods of time utilizing an ionic strength buffer of ammonium chloride and ammonium hydroxide. Of the two buffer systems studied, the pH 9 system appeared to be superior.

Nitrate

It has been demonstrated that nitrate concentrations in excess of 45 mg/ℓ were directly related to a temporary blood disorder in infants called methemoglobinemia.[51] Nitrates are, therefore, routinely monitored as a health precaution. Historically, except for some well water sources, nitrate concentrations have usually been considerably under the toxic level and there wasn't too much concern. However, changes in farming techniques and irrigation have resulted in substantially higher nitrate concentrations in the farm runoffs and eventually higher nitrate concentrations in the source of the drinking water. Although still under the 45 mg/ℓ level, the elevated nitrate levels promote algae growth in some reservoirs with the resulting customer complaints. The result of higher nitrate concentrations was that the water utilities were interested in monitoring nitrates for their own considerations as well as the public's welfare.

Wet chemical techniques for nitrate are usually quite accurate, but very time consuming. The ion selective electrode for nitrate was capable of measuring concentrations of 45 mg/ℓ and below, and was selected for use on the Laboratory because of its versatility.

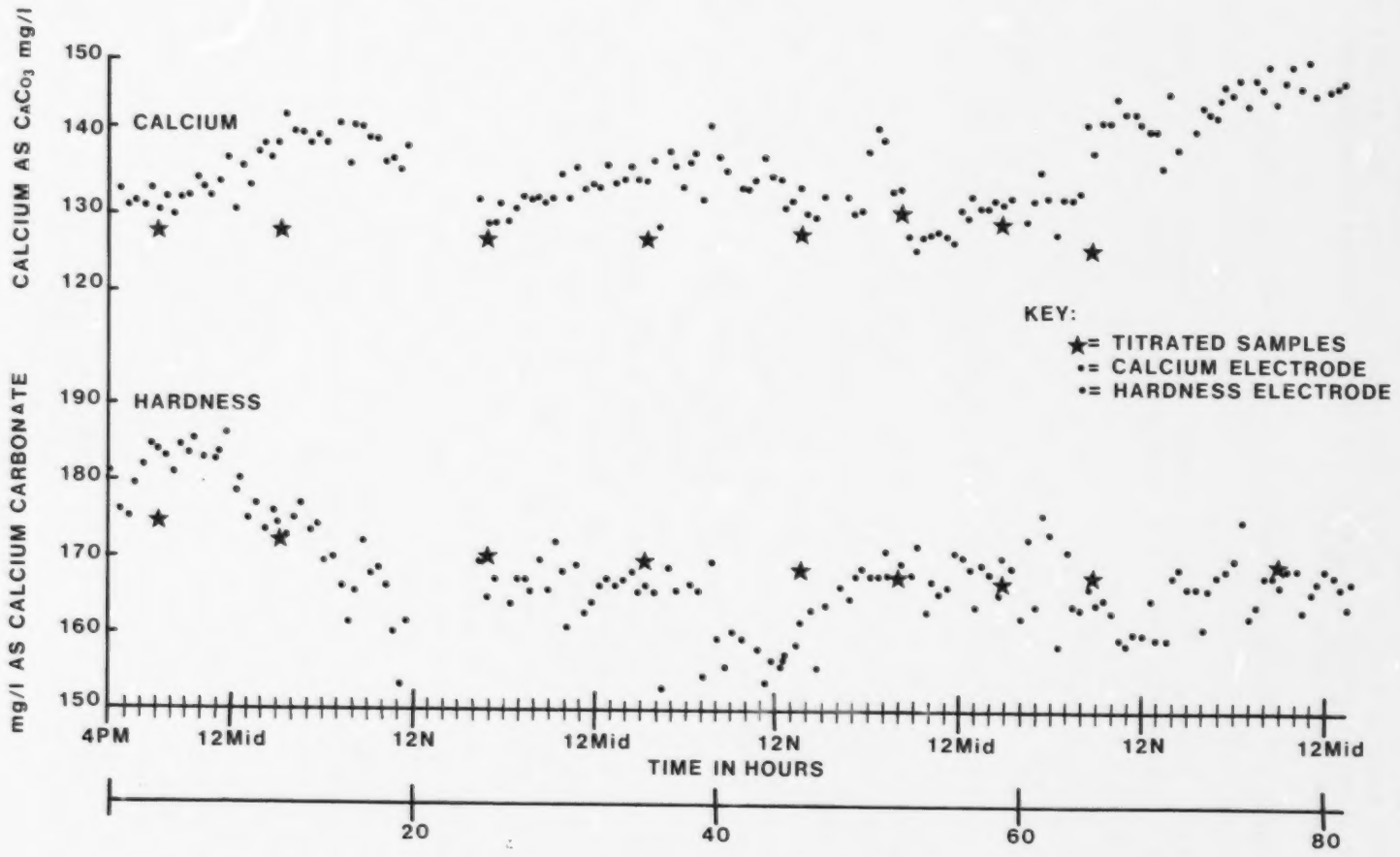

Figure 9. Performance of calcium and hardness electrodes in 0.6 moles/l ammonium chloride - ammonium hydroxide buffer as a function of time.

As with the other electrodes, a long term reliability test was conducted using repeated samples from a large reservoir of tap water. The results of the test are shown graphically in Figure X and the statistics summarized according to each calibration in Table 7.

TABLE 7. STATISTICAL RESULTS OF THE NITRATE ELECTRODE

Calibration Number	Mean mg/ℓ NO_3	Standard Deviation	Rel. Std. Deviation	Relative Error	Brucine mg/ℓ NC_3
1	3.78	0.07	2.0 %	6.5 %	3.55
2	3.62	0.07	1.9 %	9.5 %	4.00

Results of the nitrate electrode study suggest that the method was precise, but possibly lacking in accuracy. It should be pointed out that three mg/ℓ NC_3 or about 10^{-4} molar was near the lower limit of detection of the electrode.[52] Measurements at these concentrations are subject to more bias than measurements that fall in the middle of the linear response. Nitrate concentrations are not a problem until they begin to approach 40 mg/ℓ and it was thought that the ion selective electrode would perform quite well.

Free Fluoride

Fluoride additions to municipal drinking water supplies are quite common today because it has been shown that fluorides significantly reduce dental caries especially in younger children.[20,21] The accepted fluoride dosage for the beneficial effect is around 1.0 mg/ℓ, and thus any sensor utilized on the Mobile Laboratory would have to measure accurately at this level.

Crosby, et al.[22] evaluated five spectrophotometric, one titration, and the specific ion electrode methods for determining fluorides and found the electrode method surpassed all the other methods with regard to speed, accuracy and convenience. Numerous other investigators[23-31] have utilized the fluoride ion selective electrode to routinely analyze fluorides in the 1 mg/ℓ range found in municipal drinking water. Their results have shown fluoride specific ion electrodes to be accurate, and exhibit linerarily in the desired concentration areas. Armed with these facts it was determined to utilize the ion selective electrode as the sensing element for the fluoride determination.

The fluoride electrode was more stable than the calcium and hardness electrodes because the liquid junction had been replaced by a solid crystal and problems of pump pulsations didn't figure significantly in the signal. However, the electrode was still subject to drift, as were others, indicating the need for frequent standardization. A system similar to the alkalinity, hardness, and calcium was implemented because it incorporated buffer addition as well as restandardization and offered greater flexibility. There is evidence the fluorides can be determined without ionic strength buffers,[24,26]

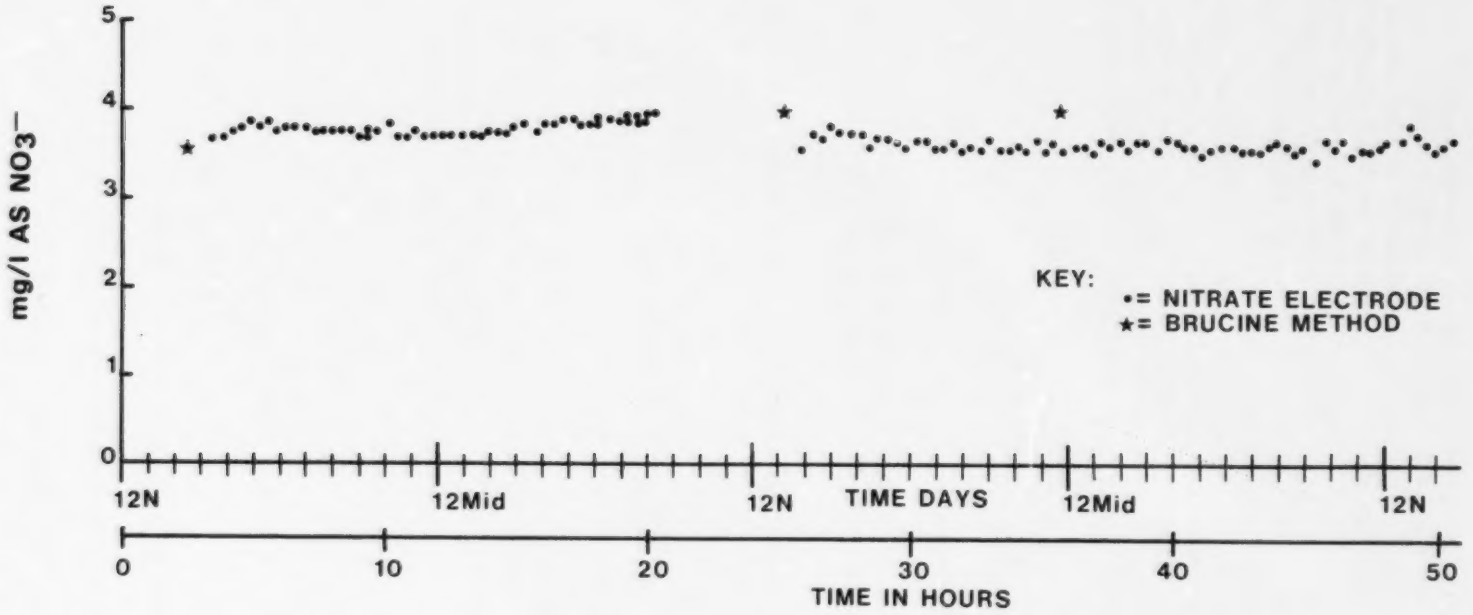

Figure 10. Performance of nitrate electrode in 0.006 molar sodium fluoride as a function of time.

but due to the constraint of traveling throughout the country it was thought to make it as general as possible and include ionic strength adjustment.

A standard of 0.1 mg/ℓ fluoride was introduced as the baseline in every sampling sequence and the tap water was compared to this standard. No problems were found in switching from standards prepared in distilled water to the samples of tap water as the ionic strength buffer masked any interferences. The buffer solution was prepared to have an ionic strength of 1.1 M and the pH adjusted to about 5.2 with sodium hydroxide.

Figure XI illustrates a calibration curve for free fluorides with the results being expressed as a difference between the calibration standard and the baseline standard. Figure XII shows the long term accuracy and reliability of the electrode. During a two day sampling period consisting of 135 samples of the same water the system performed in the following manner:

Mean	0.134 mg/ℓ
Standard Deviation	0.002
Relative STD Deviation	1.65 %

This type of test shows that the fluoride electrode can be employed in a continuous type of analyses, and yields accurate, dependable results.

Total Fluoride

It is common knowledge the fluoride ion will complex with some metals that are commonly observed in municipal drinking water, namely iron and aluminum. Therefore, it follows that there has been discussion as to the effective concentration of fluoride. To circumvent this problem, a second fluoride system was installed, and named total fluoride. The total fluoride system employs a citrate compound[24,25,27-29] that acts as a decomplexing agent for fluoride, and the net result is that the electrode sees all the fluoride in the sample.

The difference between free and total fluoride ion concentrations can be very important to treatment plant operators. When concentrations of free and total are similar, operators know their recovery techniques are working satisfactorily. Conversely, if total fluoride begins to increase the operators are alerted to a problem within the treatment system and steps can be taken to bring the system back in balance.

Figure XIII is a typical calibration curve for total fluoride with the results again being expressed as the difference between the baseline standard and the calibration standard. Figure XIV illustrates the results of a reliability test run consisting of 180 samples of the same tap water over a 72 hour period. The results of the test are summarized as:

Mean	0.150 mg/ℓ
Standard Deviation	0.002
Relative Std. Deviation	1.16 %

The data indicate the fluorides, whether free or combined can be successfully analyzed using an ion selective electrode.

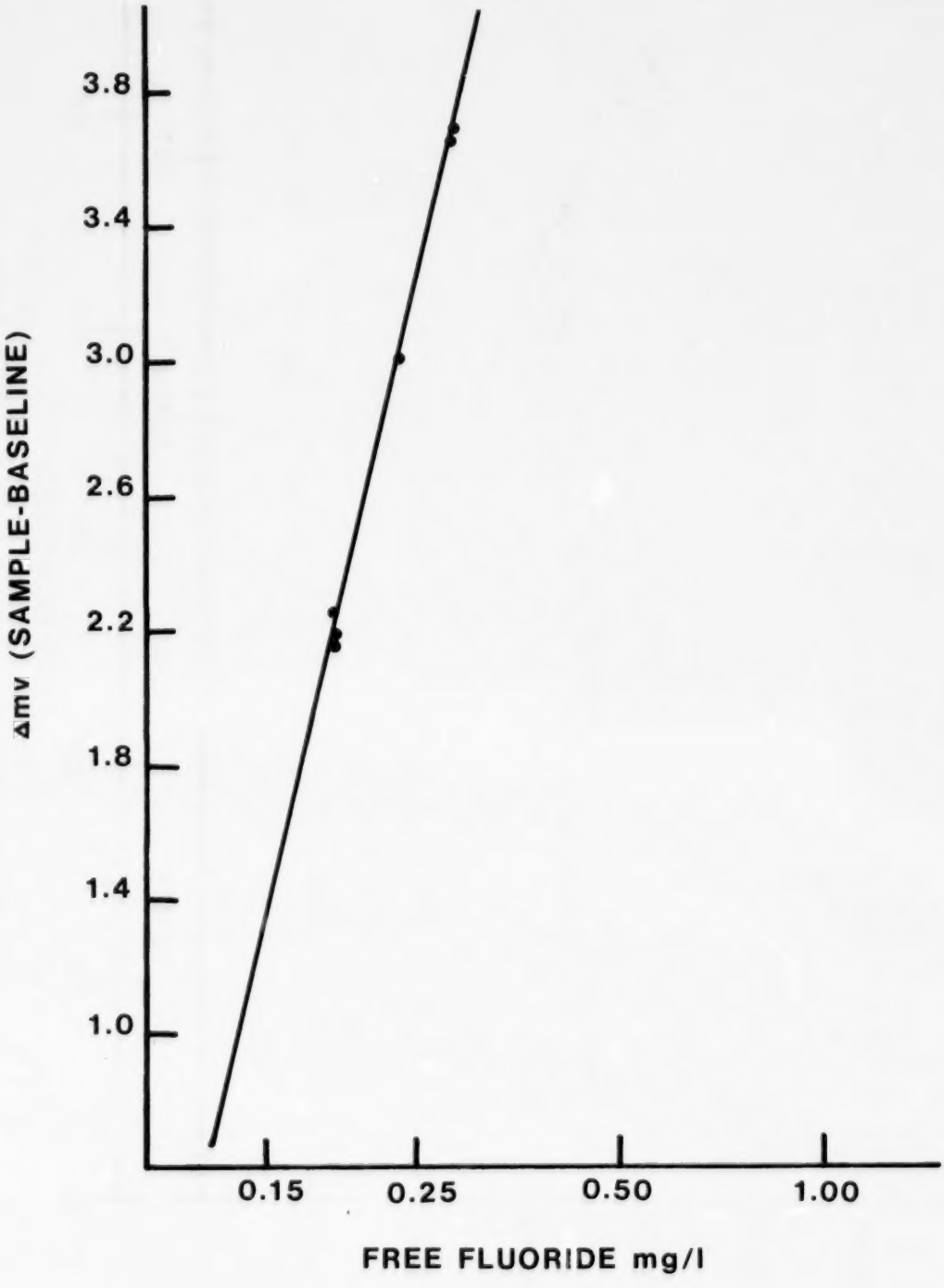

Figure 11, Free fluoride calibration curve.

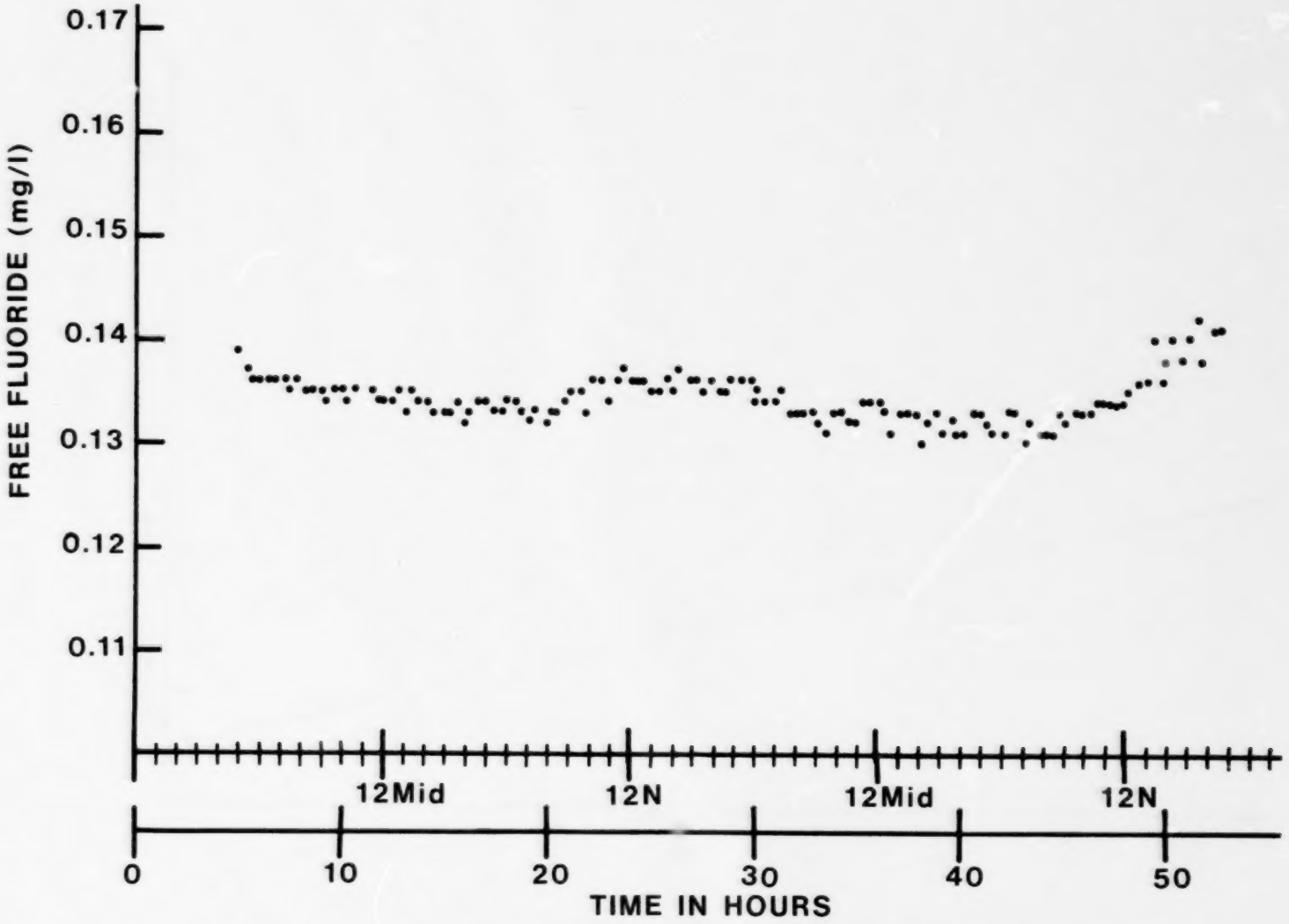

Figure 12. Performance of free fluoride electrode as a function of time.

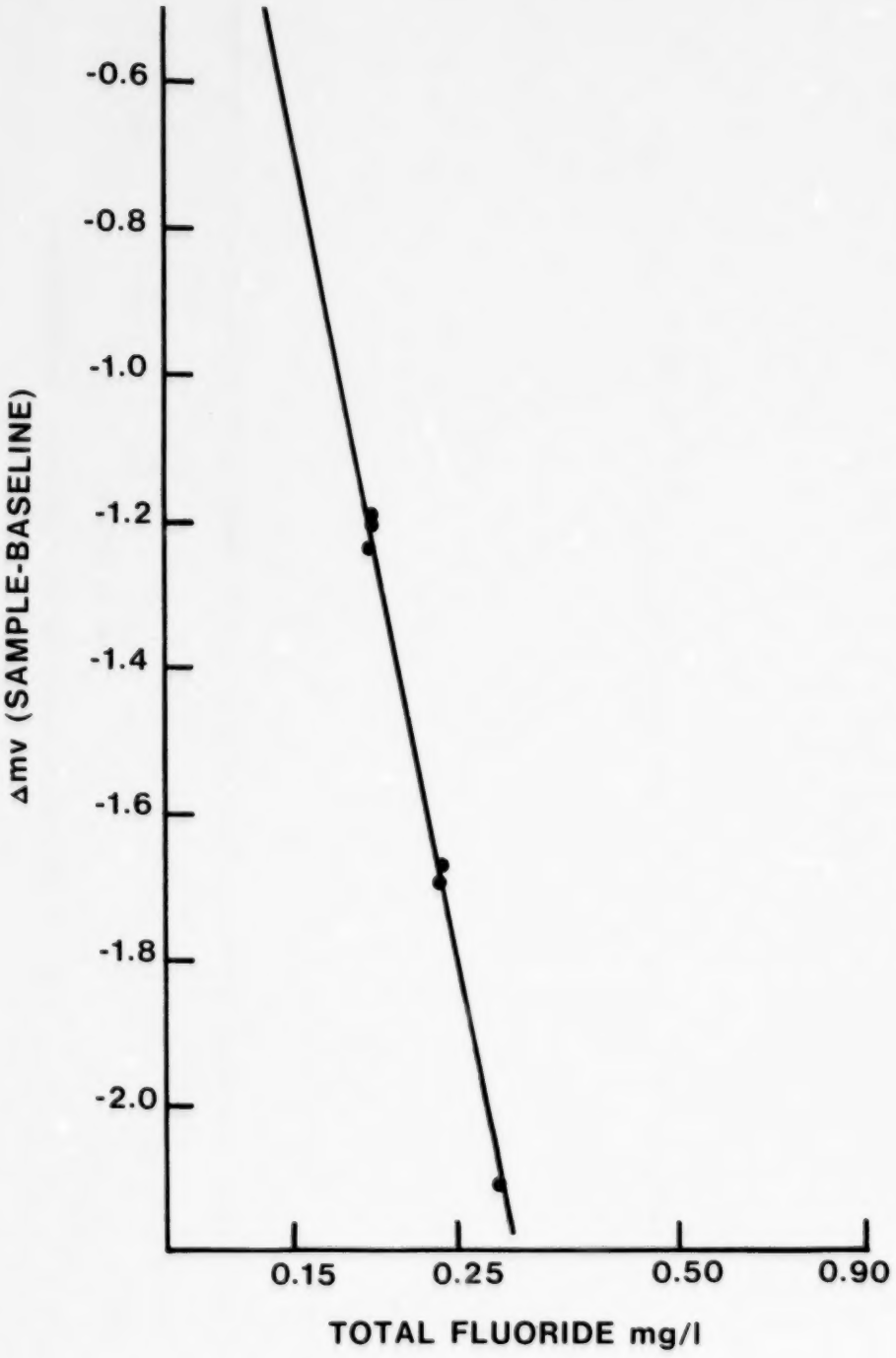

Figure 13. Total fluoride calibration curve.

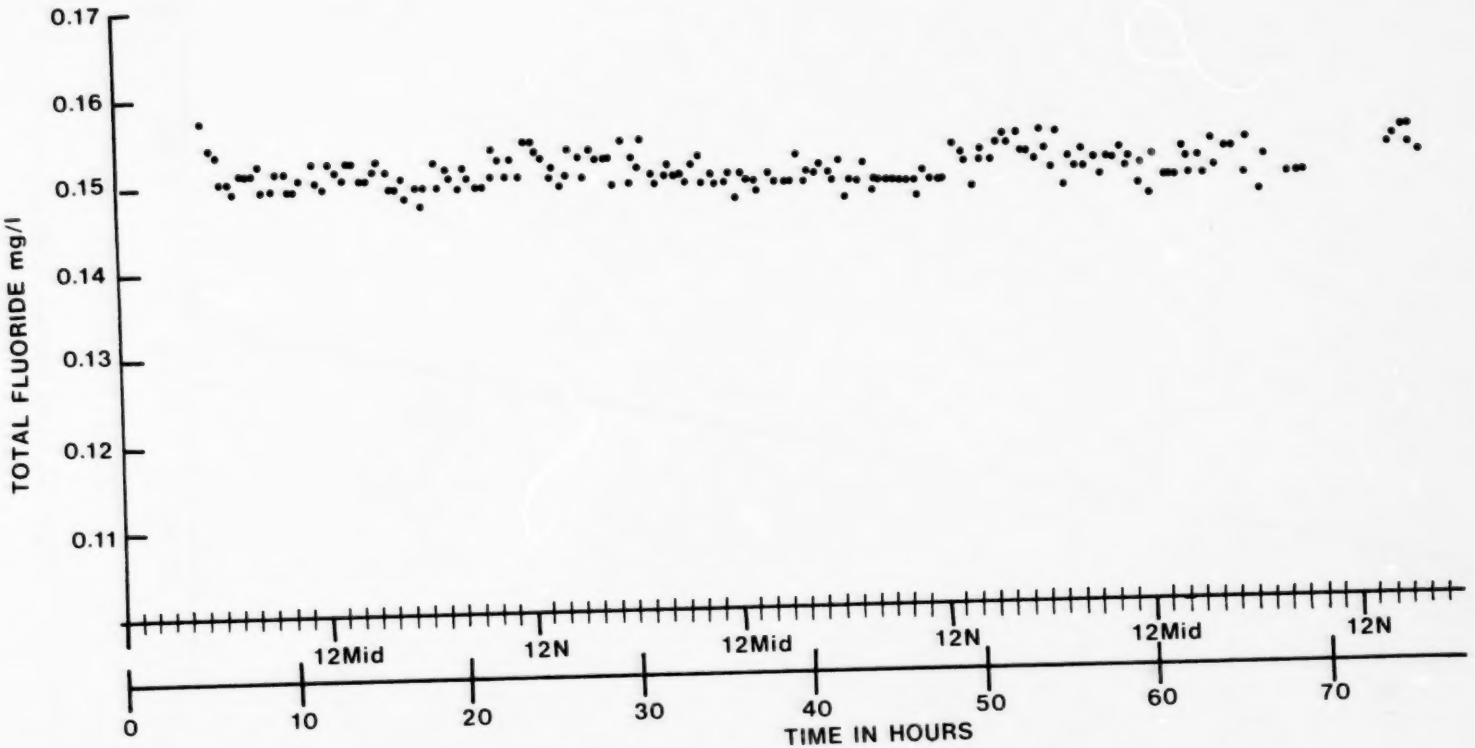

Figure 14. Performance of total fluoride electrode as a function of time.

Chloride

Water quality analysis usually have a core of parameters that are always determined and chloride is one of those parameters. Chloride ions are an indication of the general condition of the water as well as being specifically related to other parameters. In sufficiently high concentrations, chlorides can impart an objectionable taste in the water. Being one of the principle anions in drinking water, chlorides are directly related to conductivity and ionic strength, and can poison some plant life. The chloride ion has been linked with the corrosion mechanism of iron and steel,[33] and thusly are of great interest to utilities preventive maintenance programs.

In the past chlorides have been determined by titration with silver nitrate, but several alternate methods are available today. The samples and standards for the chloride determinations were done by the Mercuric Nitrate method. A specific ion electrode for chloride was employed because of its ability to analyze continuously.

The chloride electrode had no liquid junction or flexible membrane to cause problems and was installed in the Schneider Robot Stream Monitor. The electronics on the Monitor were such that zero chloride corresponded to zero millivolts output, and 240 mg/ℓ chloride corresponded to full scale or 1000 millivolts output. The electrode was calibrated accordingly. Figure XV was calibrated using standards of 25, 50 and 100 mg/ℓ chloride standards and was shown to be linear with a correlation coefficient of 0.999 and a slope of 4.14 mg/mg/ℓ. Figure XVI illustrates the electrode's response over an extended period of time. Again, after the initial calibration, the electrode response fell about 5 mg/ℓ. The system was recalibrated and performed satisfactorily for about 50 hours. Table 8 shows the statistical results for the chloride electrode's operation.

TABLE 8. STATISTICAL RESULTS FOR THE CHLORIDE ELECTRODE

Calibration Number	Mean	Standard Deviation	Relative Std. Deviation	Standard Error	Average Titration
1	31.2 mg/ℓ	1.69	5.42 %	7.11 %	33.6 mg/ℓ
2	35.3 "	0.74	2.10 "	3.64 "	34.0 "

The data indicate that the chloride electrode can be used to routinely monitor chloride ion concentrations.

pH

The oldest and most reliable electrode in the specific ion family of electrodes is the one that measures hydrogen ion activity. These electrodes have been developed for the last thirty years since the early investigators noticed the sensitivity and selectivity some glasses had for hydrogen ions. This observation had many ramifications and in fact opened a new area in potentiometry for study.

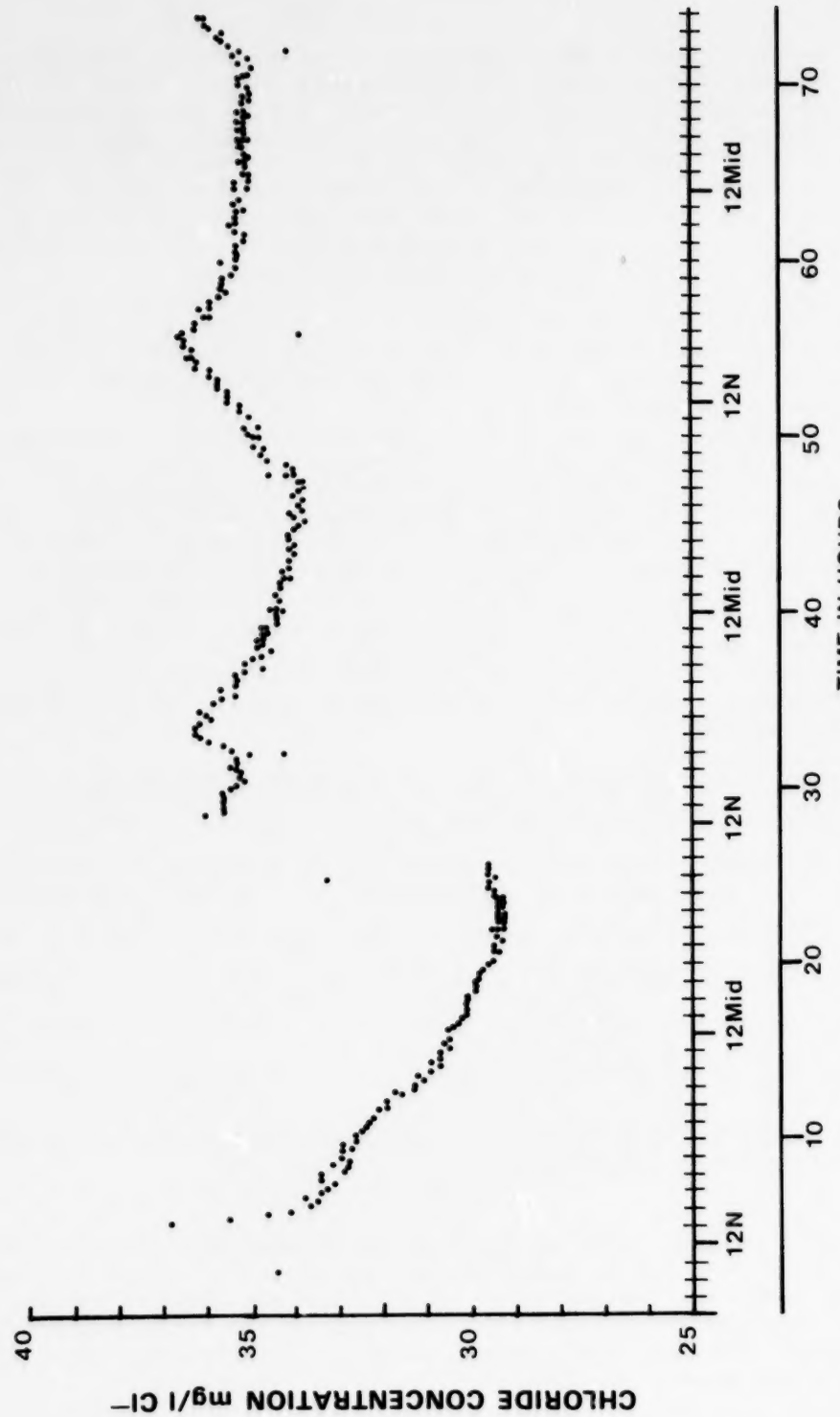

Figure 16. Performance of chloride electrode as a function of time.

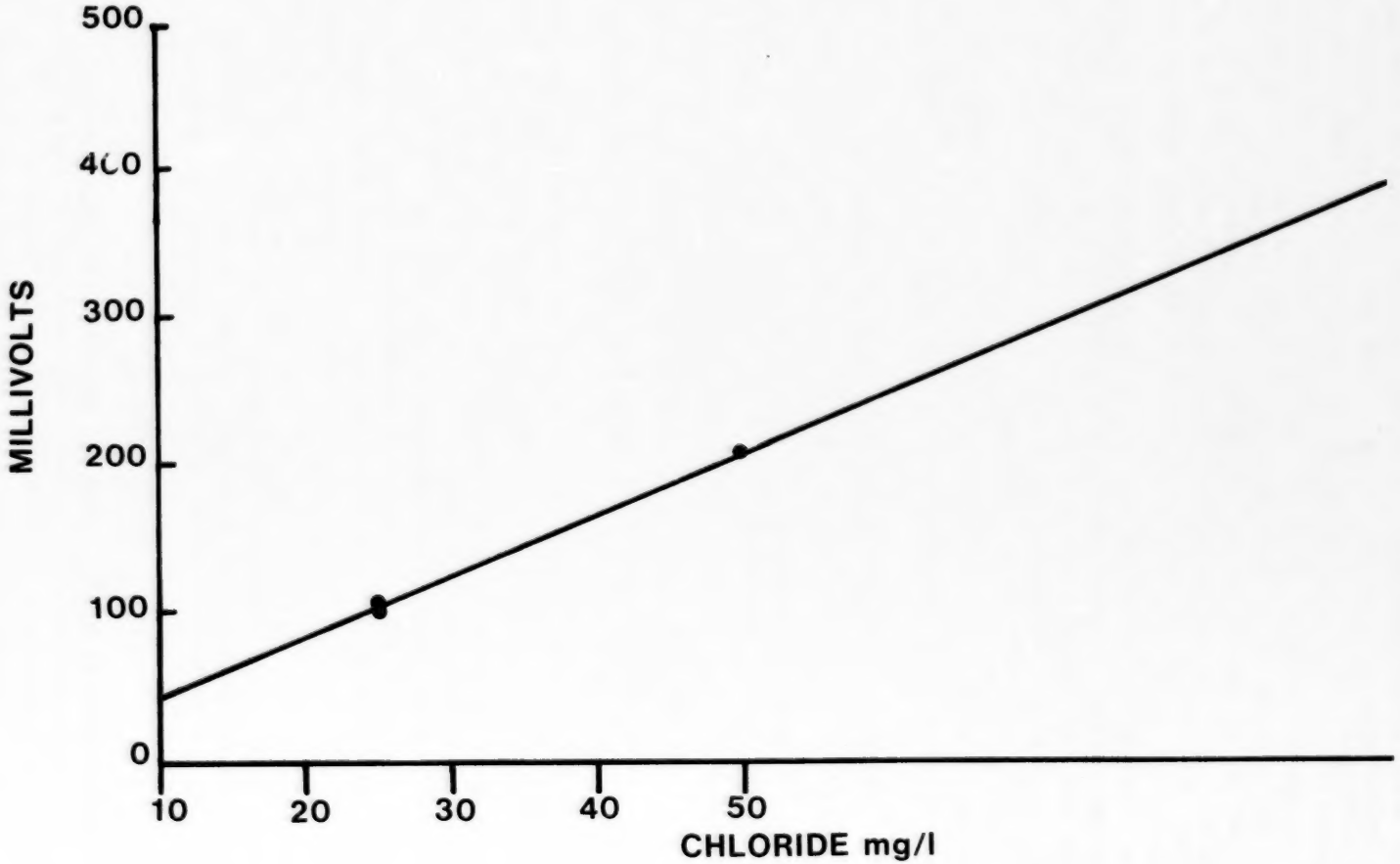

Figure 15. Calibration curve for chloride electrode.

The pH measurement associated with water quality cannot be over estimated as to its importance. The control of pH is the most important variable in treatment techniques such as coagulation and flocculation. Failure to operate within specified limits results in lower quality water and wasted chemicals. Hydrogen ion concentration is important to chlorination operations in that it influences the equilibrium of the hypochlorous acid and has an effect on the germicidal action of the chlorine. The pH plays an important role in corrosion and corrosion control by being one of the main indices of the stability of the water. All in all, pH is one of the most basic data parameters utilized on the mobile laboratory.

The pH electrode was installed in the Schneider Robot Stream Monitor in the same manner as the chloride, and with the same kind of electronics. Full scale output was 1000 millivolts for a pH of 12 or it could be calibrated using 83.33 mv/pH unit. Buffers of pH 7 and 10 were used to calibrate the system and a standard curve is illustrated in Figure XVII.

After the electrode was calibrated it was placed on tap water for an extended period of time. The results of this test are shown in Figure XVIII. The statistical results for the pH electrode are summarized in Table 9.

TABLE 9. STATISTICAL RESULTS FOR pH ELECTRODE

Calibration Number	Mean	Standard Deviation	Rel. Standard Deviation	Relative Error	Mean Lab Electrode
1	7.983	0.062	0.783 %	0.95 %	7.908

The data indicate that the pH electrode can be successfully employed to measure hydrogen ion concentrations of water for extended periods of time.

The evaluation of all the ion selective electrodes except fluoride and pH was done by comparison to a standard method. This presents a problem because some of the standard methods have a degree of uncertainty associated with them. A second problem facing electrode users was that of ion activity being different from concentration. It was impossible to calibrate the electrodes unless it was assumed that ionic activity equaled the analytical concentration. Above are two major concerns of ion selective electrode users, but if the recorded data is compared with results of Standard Method's evaluation the results are encouraging. Table 10 compares the relative standard deviations and relative errors of the electrode methods with the appropriate standard method. Examination of the results in Table 10 one finds the electrode results close to the standard methods in terms of accuracy and precision.

CONCLUSION

It has been suggested by Dr. James W. Ross Jr.[54] that ion selective electrodes are not highly accurate. To help overcome some of these problems, buffer additions and standards were added to the sampling cycle. It was shown that selection of the proper ionic strength adjustor made a significant

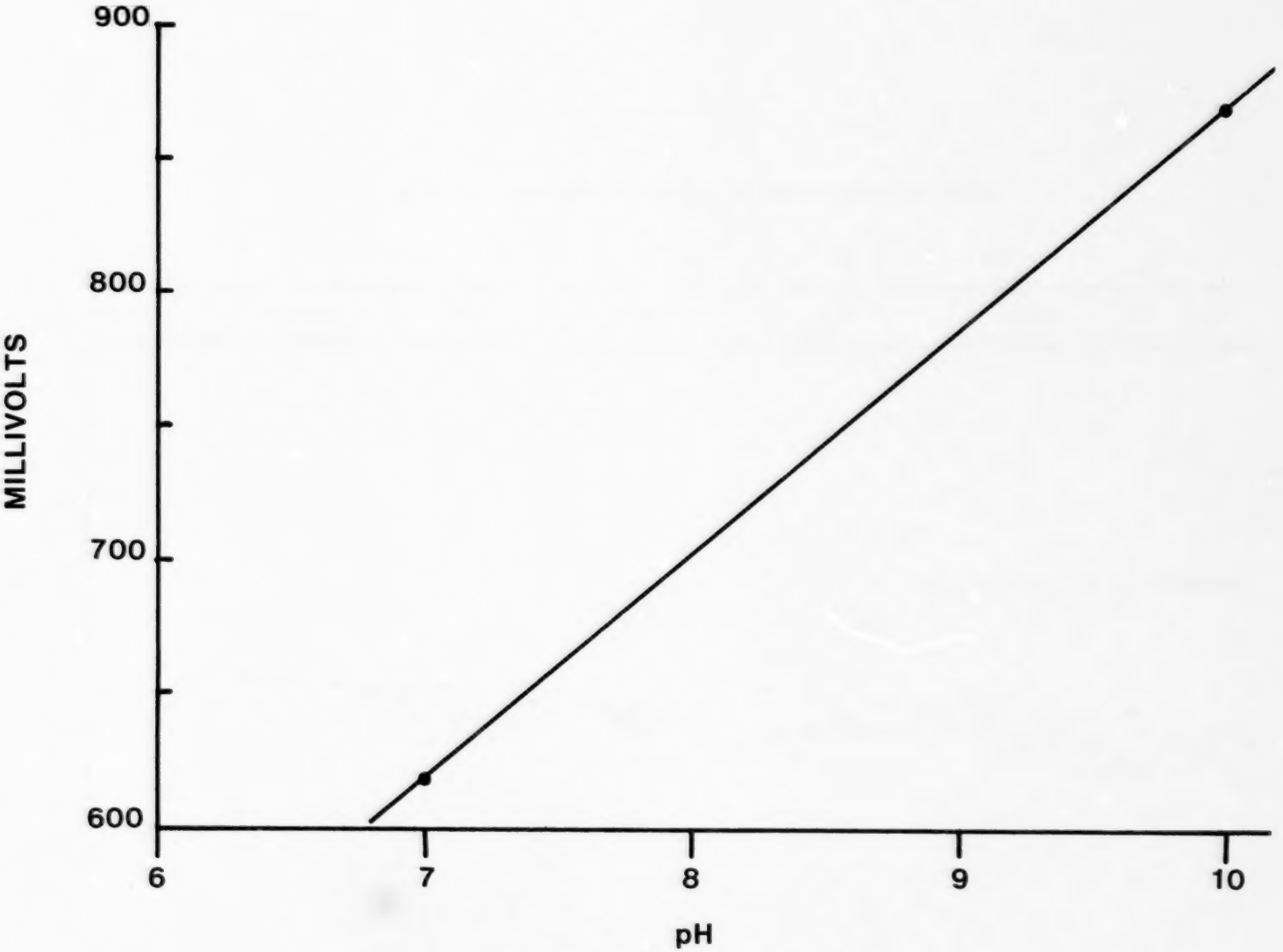

Figure 17. Calibration of pH electrode.

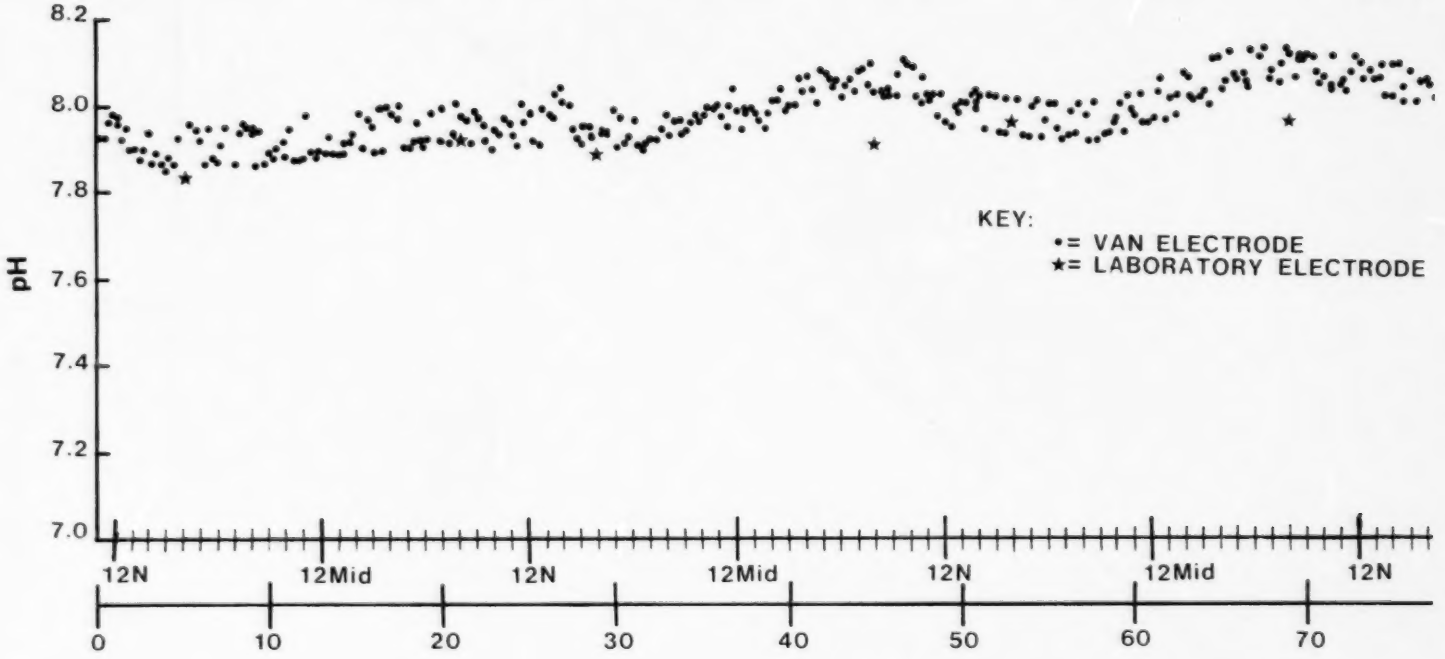

Figure 18. Performance of pH electrode as a function of time.

TABLE 10. COMPARISON OF RELATIVE STANDARD DEVIATIONS AND RELATIVE ERRORS OF THE STANDARD AND ELECTRODE METHOD

Substance Determined	Electrode Method		Standard Method	
	Rel. Std. Dev.	Rel. Error	Rel. Std.Dev.	Rel. Error
Alkalinity	3.4 %	1.6 %		
Hardness	9.7 "	10.6 "	2.9 %	0.8 %
	2.4 "	6.2 "		
pH 10.1	1.9 "	1.2 "		
	1.3 "	--		
pH 9.0	4.4 "	1.2 "		
	1.8 "	2.4 "		
Calcium	11.4 "	1.0 "	9.2 "	1.9 "
	6.7 "	0.3 "		
	3.5 "	0.4 "		
	5.8 "	--		
	2.8 "	6.3 "		
	2.5 "	4.7 "		
Nitrate	2.0 "	6.5 "	5.5 "	6.0 "
	1.9 "	9.5 "	15.4 "	4.5 "
Fluoride	1.7 "	--	3.6 "	0.7 "
Chloride	2.1 "	3.6 "	3.3 "	2.9 "
pH	0.78 "	1.0 "	--	--

difference in the operation of the hardness and calcium electrodes, and allowed continuous operation.

It was also shown that some of the more common ion selective electrodes such as hydrogen ion, fluoride ion, nitrate ion and chloride ion could be operated for prolonged periods of time in an accurate and precise manner.

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